Contractor's Report to the Board

Survey of Compost Samples for Presence of Clopyralid Herbicide

June 2005

Produced under contract by:

San Diego State University





STATE OF CALIFORNIA

Arnold Schwarzenegger Governor

Alan C. Lloyd, Ph.D. Secretary, California Environmental Protection Agency

INTEGRATED WASTE MANAGEMENT BOARD

Rosario Marin **Board Chair**

Rosalie Mulé **Board Member**

Chervl Peace Board Member

Carl Washington Board Member

Vacant **Board Member**

Vacant **Board Member**

Mark Leary Executive Director

For additional copies of this publication, contact:

Integrated Waste Management Board Public Affairs Office, Publications Clearinghouse (MS-6) 1001 | Street P.O. Box 4025 Sacramento, CA 95812-4025 www.ciwmb.ca.gov/Publications/ 1-800-CA-WASTE (California only) or (916) 341-6306

Publication #443-05-013

Copies of this document originally provided by CIWMB were printed on recycled paper containing 100 percent postconsumer fiber.

Copyright © 2005 by the California Integrated Waste Management Board. All rights reserved. This publication, or parts thereof, may not be reproduced in any form without permission.

Prepared as part of contract no. IWM-C2060 (total contract amount: \$112,144, includes other services).

The California Integrated Waste Management Board (CIWMB) does not discriminate on the basis of disability in access to its programs. CIWMB publications are available in accessible formats upon request by calling the Public Affairs Office at (916) 341-6300. Persons with hearing impairments can reach the CIWMB through the California Relay Service, 1-800-735-2929.

Join Governor Schwarzenegger to Keep California Rolling.

Every Californian can help to reduce energy and fuel consumption. For a list of simple ways you can reduce demand and cut your energy and fuel costs, Flex Your Power and visit www.fypower.com.

Disclaimer: This report to the Board was produced under contract by San Diego State University. The statements and conclusions contained in this report are those of the contractor and not necessarily those of the California Integrated Waste Management Board, its employees, or the State of California and should not be cited or quoted as official Board policy or direction.

The State makes no warranty, expressed or implied, and assumes no liability for the information contained in the succeeding text. Any mention of commercial products or processes shall not be construed as an endorsement of such products or processes.

Table of Contents

Acknowledgments	ii
Introduction	1
Clopyralid	1
Compost	1
Objective	1
Facilities Studied	2
Sample Collection	2
Sample Extraction and Analytical Method	2
Conclusions and Recommendations	2
Table 1. Clopyralid Analysis of the First Set of Compost Samples	4
Table 2. Clopyralid Analysis of the Second Set of Compost Samples	5
Table 3. Clopyralid Analysis of the Third Set of Compost Samples	6
Figure 1. Clopyralid Concentration in Compost Samples	7
Table 4. Comparison of Clopyralid Concentrations	7
Table 4. Comparison of Clopyralid Concentrations	8
Ribliography	9

Acknowledgments

The authors acknowledge contributions of the California Department of Food and Agriculture (CDFA) in performing in-kind services for this project, including collection, packaging, and mailing of compost samples to Morse Laboratories, Inc. CDFA also distributed the clopyralid sampling form to compost operators, collected completed forms, and forwarded them to Morse Laboratories, Inc. Stephen Beam and Pierre Labossiere directed staff in the collection of compost samples. Funding for this project was provided by the California Integrated Waste Management Board (CIWMB) under Contract No. IWM-C2060. Brenda Smyth and Brian Larimore of the CIWMB were the contract managers for this project. Morse Laboratories, Inc. extracted and analyzed compost samples.

Introduction

Clopyralid

Clopyralid is a growth regulator herbicide used for control of broadleaf weeds such as yellow star thistle, dandelion, and clover. It works by mimicking growth hormones called auxins, and it causes abnormal growth. Clopyralid is a pyridine carboxylic acid type herbicide with chlorine substitutions (3,6-dichloro-2-pyridine carboxylic acid). It is the active ingredient of many herbicide formulations including Transline, Stinger, Confront, and Lontrel. Also, clopyralid is an ingredient in some Andersons lawn fertilizers and Riverdale products designed for landscape and golf course uses. Pyridine carboxylic acid type pesticides including clopyralid have been shown to cause severe damage to susceptible plants at concentrations as low as 10 parts per billion (pbb) or even less in the finished compost (Bezdicek, 2001). Although clopyralid does not affect most plants at these concentrations, some are unusually susceptible, including peas, potatoes, tomatoes, peppers, and sunflowers.

Compost

Composting is an integral component of waste diversion and is widely used as a low-cost, low-maintenance treatment method for almost all types of organic waste streams. Composting is a biological process through which organic matter is converted to humus-like material by a diverse consortium of microorganisms. Composting takes the nuisance materials and converts them to a useful and marketable product. In 2002, the California Integrated Waste Management Board (CIWMB) and composting industry recognized a potential threat from clopyralid to the success of municipal waste recycling operations throughout California.

The detection of clopyralid residues in compost brought this potential threat to the attention of the state's compost stakeholders. The first incident involving clopyralid in yard trimmings was reported in Spokane, Washington. A commercial greenhouse that grows tomatoes, marigolds, dusty miller, and parsley had experienced substantial damage to their produce in the 1999–2000 growing season. The observed damage included poor and deformed growth, leaf curling, and twisted and bent stems. The investigation revealed that the damage was caused by clopyralid residues present in compost that was applied onto the growing beds (Rynk, 2000). There are still 25,000 cubic yards of unsold compost remaining on the facility due to clopyralid residues. This incident cost the composting facility an estimated \$250,000.

The city of Christchurch in New Zealand has reported detection of increasing levels of clopyralid in its compost (Fietje, 2001). Grass clippings treated with clopyralid were identified as the main source of contamination. Another incidence was reported by Pennsylvania State University (Houck and Burkhart, 2001). The university has been composting landscape debris, dining commons food residuals, and dairy manure since 1997. In the spring of 2000, the compost began to be used for vegetable crop research for the first time. Researchers noticed crop damage similar to other incidences. The investigations revealed that clopyralid was again the culprit. Testing by some California compost operations during late 2001 and 2002 detected low levels of clopyralid in compost.

Objective

The objective of this project was to evaluate various finished compost products from different composting facilities located throughout California for the presence of clopyralid herbicide.

Facilities Studied

A total of 15 yard waste composting facilities were surveyed. Facilities were chosen to represent the main composting regions of California (that is, Bay Area, Central Valley, Central Coast, and Southern). For proprietary reasons, the names of the facilities are not identified, but they are assigned facility ID numbers. The sampling occurred between the fall of 2003 and fall of 2004 with three samplings from each facility. The first sampling took place in late October and early November, 2003. The second samples were collected in late August and early September of 2004, and the final sampling was in late October and early November 2004. While the majority of the facilities were composting only yard waste, several of them had other feedstock materials such as manure and mushroom bedding incorporated into their blends.

Conclusions on the role of specific feedstocks on clopyralid residue levels could not be made since site operators provided incomplete data on the types of feedstock composted. The types and the percentages of the feedstock materials are provided in Tables 1 through 3. The active composting and curing periods have shown a large variation between facilities and the sampling times as presented in Tables 1 through 3.

Sample Collection

California Department of Food and Agriculture personnel collected composite samples by mixing 12 random grab samples. The grab sampling scheme included four samples, each collected at a different cross-section, taken from the sections of one-half, one-fourth, and one-eight the width of the pile. The grab samples were thoroughly mixed in a 5-gallon plastic bucket. From this mixture, a 1-gallon ziplock bag was filled to make a composite sample. The sample was placed in a second 1-gallon ziplock plastic bag and placed in insulated containers packed with ice packs or blue ice for shipment to Morse Laboratories within 24 hours of collection. In order to prevent samples from possible contamination, tools, buckets, and equipment were cleaned with alcohol rinse.

Sample Extraction and Analytical Method

Morse Laboratories extracted and analyzed samples by following Method-151, which they developed for the determination of clopyralid in compost, grass, and similar matrices with a detection limit of 1 ppb. The details of the sample extraction and analytical method are not available due to proprietary reasons.

Conclusions and Recommendations

This project was a limited study of clopyralid residues detected in compost sampled from a small number of compost facilities. Clopyralid concentrations in compost samples range from 6.40 ppb to less than 1 ppb, which is the method detection limit. In the first sampling, the highest concentration was 6.40 ppb; four samples exhibited concentrations below the detection limit of 1 ppb (Table 1). The second set of samples as presented in Table 2 showed that the highest concentration was 5.01 ppb, while the number of samples below the detection limit increased to eight. In the final sampling, nine facilities were below the detection limit and the highest concentration was 2.75 ppb (Table 3).

Due to the lack of data, the analysis of the results did not yield any significant pattern either in terms of the effect of addition of other feedstock into the composting blends or the maturity of the composts. Since the concentrations of the clopyralid in the feedstock materials were not determined, we were unable to make such conclusions. The few facilities with the clopyralid concentrations followed no particular trend, though a pattern of general decrease appeared. Figure 1 shows the cumulative concentrations reported from 15 facilities. These were 28.42 ppb, 17.13 ppb, and 11.14 ppb for the first, second, and final sampling, respectively. The number of non-

detects, that is, the concentration below the detection limit, have increased from 4 to 8, and to 9 from first sampling to second, and to the third sampling. (In other words, there were 4 non-detects for the first sampling, 8 non-detects for the second, and 9 for the third.) These figures suggest that the presence of clopyralid in finished compost products is becoming less of a concern over time.

The clopyralid monitoring data suggests that clopyralid concentrations in finished products are decreasing and, thus, becoming less of a concern over time.

Table 1. Clopyralid Analysis of the First Set of Compost Samples

Sam	ple		Feedst	Maturity		Clopyralid				
ID	Date	Yard Waste	Manure	Food	Mushroom Bedding	Fish	Paper & Cardboard	Compost	Curing	Concentration (ppb)
Fac. No. 1	10/23/03	100						50 d	30 d	<1
Fac. No. 2	10/28/03	60	10 [*]		30			60 d	45–60 d	<1
Fac. No. 3	10/23/03	✓					✓	100 d	90 d	<1
Fac. No. 4	10/27/03	100						1 w	<6 wk	2.86
Fac. No. 5	10/30/03	97	3**					15 d	60–90 d	3.38
Fac. No. 6	10/30/03			<1			<1	6 m	1 m	3.48
Fac. No. 7	10/27/03	100						1 w	15 w	1.15
Fac. No. 8	10/29/03	100						80 d	7–120 d	<1.0
Fac. No. 9	10/30/03	100						>4 m	>2 m	1.0
Fac. No. 10	10/30/03	95		2			3	4–6 m	2 m	1.25
Fac. No. 11	10/30/03	100						4 m	2 m	6.4
Fac. No. 12	11/14/03	100						na	Na	2.02
Fac. No. 13	11/5/03	100						60 d	15 d	3.58
Fac. No. 14	10/23/03	98		1		1		8 m	2m	1.05
Fac. No. 15	11/5/03	100						60	30	2.25

^{*}Dried poultry waste

na: not available

^{**}Cow, horse, and goat manure

Table 2. Clopyralid Analysis of the Second Set of Compost Samples

Sam	ple		Feedst	Maturity		Clopyralid				
ID	Date	Yard Waste	Manure	Food	Mushroom Bedding	Fish	Paper & Cardboard	Compost	Curing	Concentration (ppb)
Fac. No. 1	8/30/04	100						60 d	50 d	5.01
Fac. No. 2	8/31/04	✓			✓		✓	2–4 m	2 m	<1
Fac. No. 3	8/30/04	100						90 d	75 d	<1
Fac. No. 4	8/31/04	100						6 wk	6 d	1.08
Fac. No. 5	8/30/04	✓	✓					6 m	2 m	1.17
Fac. No. 6	8/30/04	100						8 m	2 m	1.99
Fac. No. 7	8/31/04	100						14 wk	2 wk	<1
Fac. No. 8	8/31/04	100						80 d	12 d	<1
Fac. No. 9	8/30/04	100						4–6 m	2 m	2.18
Fac. No. 10	8/30/04	97		1			2	5 m	ns	<1
Fac. No. 11	8/30/04	100						6 m	6 m	<1
Fac. No. 12	8/26/04	100						>120 d	90–120 d	1.61
Fac. No. 13	9/9/04	Na						na	Na	4.09
Fac. No. 14	8/30/04	100						3 m	1 m	<1
Fac. No. 15	9/09/04	Na						na	Na	<1

na: not available

Table 3. Clopyralid Analysis of the Third Set of Compost Samples

Sample			Feedst	Maturity		Clopyralid				
ID	Date	Yard Waste	Manure	Food	Mushroom Bedding	Fish	Paper & Cardboard	Compost	Curing	Concentration (ppb)
Fac. No. 1	10/28/04	100						60 d	50 d	<1
Fac. No. 2	10/27/04	90		10				5 m	3 m	<1
Fac. No. 3	10/28/04	100						90	75	<1
Fac. No. 4	10/26/04	100						14 d	14 d	<1
Fac. No. 5	10/26/04	100						21–28 d	75–100 d	<1
Fac. No. 6	10/26/04	100						10 m	>365 d	1.66
Fac. No. 7	10/27/04	100						19 w	3 w	1.84
Fac. No. 8	10/28/04	100						80 d	7–120 d	<1
Fac. No. 9	10/28/04	100						>4 m	2–3 m	1.07
Fac. No. 10	10/28/04	100						7 m	6 wk	<1
Fac. No. 11	10/28/04	100						>4 m	>2 m	1.72
Fac. No. 12	11/01/04	100						>120 d	>90 d	2.10
Fac. No. 13	11/02/04	100						78 d	na	2.75
Fac. No. 14	10/21/04	100						3 m	15–30 d	<1
Fac. No. 15	11/01/04	100						2–3 m	1–2 m	<1

Figure.1 Clopyralid Concentration in Compost Samples

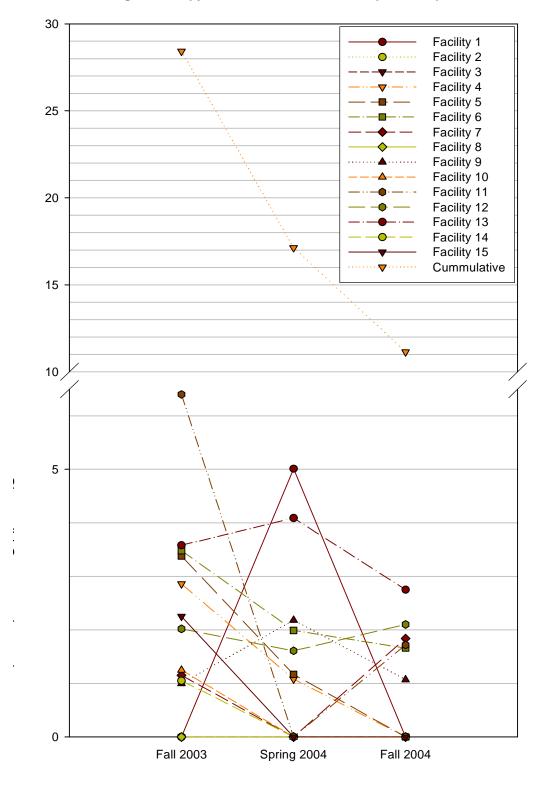


Table 4. Comparison of Clopyralid Concentrations

Facility ID	Clopyralid Concentration (ppb)							
	Fall 2003	Spring 2004	Fall 2004					
Fac. No. 1	<1	5.01	<1					
Fac. No. 2	<1	<1	<1					
Fac. No. 3	<1	<1	<1					
Fac. No. 4	2.86	1.08	<1					
Fac. No. 5	3.38	1.17	<1					
Fac. No. 6	3.48	1.99	1.66					
Fac. No. 7	1.15	<1	1.84					
Fac. No. 8	<1.0	<1	<1					
Fac. No. 9	1.0	2.18	1.07					
Fac. No. 10	1.25	<1	<1					
Fac. No. 11	6.4	<1	1.72					
Fac. No. 12	2.02	1.61	2.10					
Fac. No. 13	3.58	4.09	2.75					
Fac. No. 14	1.05	<1	<1					
Fac. No. 15	2.25	<1	<1					
Cumulative	28.42	17.13	11.14					
# of Non-Detect	4	8	9					

Bibliography

- D. Bezdicek et al., "Persistent Herbicides in Compost," *Biocycle*, July 2001, pp. 25–30.
- D. Bezdicek et al., "New Threats from Persistent Herbicides," *Agrichemical and Environmental News*, October 2000, Vol. 174, pp. 9–13.
- G. Fietje, "New Zealand City Confronts Contamination," Biocycle, July 2001, p. 31.
- N.J. Houck and E.P. Burkhart, "Penn State Research Uncovers Clopyralid in Compost," *Biocycle*, July 2001, pp. 32–33.
- R. Rynk, "Understanding the Issues: Dealing with Herbicide Residues in Compost," *Biocycle*, September 2000, pp. 42–47.